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SEPARATION METHOD OF LONG-CHAINED MONOMETHYL PARAFFINS

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Detailed explanation of the invention

The present invention relates to a method for selectively separating and recovering a high-purity long-chained paraffin from petroleum fractions containing monomethyl paraffins with carbon atoms greater than or equal to 9 but less than 20.

Monomethyl paraffins with a relatively short carbon chain such as 2-methylbutane, 2-methylpentane, etc., among monomethyl paraffins, are separated at a relatively pure state, but an industrial separation method of high-purity long-chained monomethyl paraffins with carbon chains greater than or equal to 9 has not yet been established. The long-chained monomethyl paraffins are important as various solvents such as paint solvents, polymerization solvents, aerosols, etc., and the establishment of an industrial and economical separation method for the long-chained monomethyl paraffins has been desired.

It is effective to utilize the urea adduction reaction in the separation of long-chained monomethyl paraffins. However, since generally linear paraffins coexist in petroleum fractions containing monomethyl paraffins, both paraffins form urea adducts by a urea adduction reaction, and long-chained monomethyl paraffins cannot be selectively separated. Moreover, since the stability of urea adducts of linear paraffins is far higher than the stability of urea adducts of long-chained monomethyl paraffins, the linear paraffins preferentially form urea adducts and thus long-chained monomethyl paraffins cannot be selectively separated and recovered in a pure state by the urea adduction reaction.

The present invention established a method for effectively separating long-chained monomethyl paraffins at high purity by combining the separation method by the aforementioned urea adduction reaction and the separation method by molecular sieves as described below.

Namely, the present invention is to selectively separate and recover pure long-chained monomethyl paraffins from a petroleum fraction containing long-chained paraffins with carbon numbers greater than or equal to 9 but less than 20 by adding urea of a small amount, with respect to urea adduct-forming components in the petroleum fraction, to the petroleum fraction to carry out the urea adduction reaction and remove a part of linear paraffins as urea adducts, adding an excess amount of urea, with respect to the urea adduct-forming components, to the residual liquid, wherein the existing ratio of long-chained monomethyl paraffins to linear paraffins is high, to again carry out the urea adduction reaction, carrying out the adduct decomposition and solid-liquid separation of obtained urea adducts to obtain a long-chained

monomethyl paraffin-rich paraffin mixture, and passing the mixture through a column packed with crystalline zeolite molecular sieves having an average pore diameter of 5 Å (hereinafter referred to as MS-5A) to adsorb only linear paraffins.

As described above, in the present invention, first, urea of a very low amount, with respect to urea adduct-forming components in the raw oil, is added to raw oil to carry out the urea adduction reaction so that a part of linear paraffins is removed as urea adducts by paying attention to the fact that when the urea adduction reaction is carried out in raw oils containing linear paraffins and long-chained monomethyl paraffins before reaching the final separation process by molecular sieves, the linear paraffins preferentially form urea adducts. By this, the ratio of existing long-chained monomethyl paraffins to the linear paraffins in the remaining liquor is raised so that the fraction enriched with long-chained monomethyl paraffins, as compared with the raw oil, remains. Then, an excess amount of urea for urea adduct-forming components in the residual liquor is added to the residual liquor to carry out the urea adduction reaction to form urea adducts of linear paraffins and long-chained monoalkyl paraffins, and it is subjected to adduct decomposition and solid-liquid separation to separate into a long-chained monomethyl paraffin-rich paraffin mixture and urea.

Since long-chained monomethyl paraffins obtained by the above manner contain linear paraffins as impurities, the long-chained monomethyl paraffins are passed through an MS-5A-packed tube or column to remove the linear paraffins by adsorption to obtain pure long-chained monomethyl paraffins. Furthermore, the treatment by molecular sieves may be carried out by any method for adsorption of linear paraffins.

Raw oils applicable to the present invention are all petroleum fractions containing monomethyl paraffins, but it is necessary to react monomethyl paraffins in raw oils with urea to form urea adducts. Accordingly, they are those with carbon numbers greater than or equal to 9 but less than 20, moreover those are preferred wherein methyl group is positioned relatively close to the end, namely where the methyl group is positioned at the 2, 3, or 4 carbon of the carbon chain. However, since it is also related with the length of the main chain having a methyl side chain, it is essentially regulated by the stability of urea adducts of monomethyl paraffins.

According to the present invention, as it is clear from the following application example, long-chained monomethyl paraffins having an extremely high purity can be separated and recovered, and its industrial and economical effect is extremely distinct.

Next, the present invention is explained in detail by an application example.

Application example

47 kg urea and 0.8 L methanol were added to 100 kg raw oil containing 6.5 wt% 2-methyl paraffin and 3-methyl paraffin and 20.0 wt% linear paraffins, which was kerosine oil

having boiling point range of 163-233°C and specific gravity (d_4^{15}) = 0.788, obtained from the Middle East crude oil, and the urea adduction reaction was carried out to separate 13.5 kg urea adduct containing linear members. The linear members were analyzed to confirm that the linear members consisted of 13.23 kg linear paraffins and 0.27 kg long-chained monomethyl paraffins, and thus it is comprehended that the remaining liquid contained 6.77 kg linear paraffin and 6.23 kg long-chained monomethyl paraffin. Then, 50 kg urea was added to the remaining liquid to carry out the urea adduction reaction at -10°C, and the resulting adduct was decomposed to obtain 12.74 kg of a long-chained monomethyl paraffin-rich mixture.

Then, the paraffin mixture was passed though a column packed with MS-5A, which was pre-fired at 400°C for 6 h, and heated to 180°C to obtain 6 kg of a non-adsorption effluent. It was confirmed by gas chromatography and mass spectra that the effluent consisted of 92 wt% 2-methyl paraffin, 7 wt% 3-methyl paraffin, and 1 wt% other monomethyl paraffin.

Scope of patent claim

A separation method of long-chained monomethyl paraffins, characterized in that urea at a very low amount, with respect to the urea adduct-forming components in the fraction, to a petroleum fraction containing long-chained monomethyl paraffins with carbon numbers greater than or equal to 9 but less than 20 to carry out the urea adduction reaction to separate a part of linear paraffins as urea adducts, and an excess amount of urea, with respect to urea adduct-forming components, is added to the remaining liquor to again carry out the urea adduction reaction to obtain urea adducts, which are subjected to adduct decomposition and solid-liquid separation to obtain a long-chained monomethyl paraffin-rich mixture, and then the mixture is passed through a MS-5A-packed column to adsorb linear paraffins only to separate and recover long-chained monomethyl paraffins as a non-adsorption effluent.